

## CLAIMS

We claim:

1. A method of making a vinyl polymer hydrogel having a desired physical property comprising the steps of:
  - 5 providing a vinyl polymer solution comprising a vinyl polymer dissolved in a first solvent;  
mixing the vinyl polymer solution with a gellant, wherein the resulting mixture has a higher Flory interaction parameter than the vinyl polymer solution;
  - 10 inducing gelation of the mixture of vinyl polymer solution and gellant;  
controlling the gelation rate to form a viscoelastic solution wherein workability is maintained for a predetermined period, thereby making a vinyl polymer hydrogel having the desired physical property.
- 15 2. The method of claim 1 wherein the step of providing a vinyl polymer solution includes the step of dissolving the vinyl polymer in the first solvent.
3. The method of claim 1 further comprising the step of:  
heating the vinyl polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl polymer.
- 20 4. The method of claim 3 wherein the step of mixing the vinyl polymer solution with a gellant precedes the step of heating the vinyl polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl polymer.
- 25 5. The method of claim 1 wherein the desired physical property is at least one of light transmission, gravimetric swell ratio, shear modulus, load modulus, loss modulus, storage modulus, dynamic modulus, compressive modulus, cross-linking and pore size.

6. The method of claim 1 wherein the desired physical property is physical cross-linking.
7. The method of claim 1 wherein the vinyl polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl pyrrolidone and mixtures thereof.
8. The method of claim 7 wherein the vinyl polymer is highly hydrolyzed polyvinyl alcohol of about 50 kg/mol to about 300 kg/mol molecular weight.
9. The method of claim 7 wherein the vinyl polymer is highly hydrolyzed polyvinyl alcohol of about 100 kg/mol molecular weight.
10. The method of claim 1 wherein the vinyl polymer solution is about 1 weight percent to about 50 weight percent solution of polyvinyl alcohol based on the weight of the solution.
11. The method of claim 1 wherein the vinyl polymer solution is about 10 weight percent to about 20 weight percent solution of polyvinyl alcohol based on the weight of the solution.
12. The method of claim 1 further comprising the step of contacting the viscoelastic solution with a gellant.
13. The method of claim 1 wherein the gellant is active when mixed with the vinyl polymer solution.
14. The method of claim 1 wherein the gellant is inactive when mixed with the vinyl polymer solution.
15. The method of claim 14 wherein the step of inducing gelation of the viscoelastic solution includes the step of activating the gellant.

16. The method of claim 1, wherein the Flory interaction parameter of the mixture of vinyl polymer solution and gellant ranges from 0.25 to 1.0.
17. The method of claim 1 wherein the Flory interaction parameter of the mixture is about 0.25 to about 0.5.
- 5 18. The method of claim 1 wherein the Flory interaction parameter of the mixture is at least 0.5.
19. The method of claim 1 wherein the first solvent is selected from the group consisting of deionized water, dimethyl sulfoxide, an aqueous solution of a C1 to C6 alcohol and mixtures thereof.
- 10 20. The method of claim 1 wherein the gellant is selected from the group consisting of salts, alcohols, polyols, amino acids, sugars, proteins, polysaccharides, aqueous solutions thereof, and mixtures thereof.
- 15 21. The method of claim 20 wherein the gellant is selected from the group consisting of chondroitin sulfate, dermatan sulfate, hyaluronic acid, heparin sulfate and mixtures thereof.
22. The method of claim 20 wherein the gellant is selected from the group  
20 consisting of biglycan, syndecan, keratocan, decorin, aggrecan and mixtures thereof.
23. The method of claim 20 wherein the gellant is an alkali metal salt.
24. The method of claim 23 wherein the alkali metal salt is sodium chloride.
- 25 25. The method of claim 20 wherein the gellant is an aqueous solution of sodium chloride from about 1.5 molar to about 6.0 molar.

26. The method of claim 20 wherein the gellant is an aqueous solution of sodium chloride from about 2.0 molar to about 6.0 molar
27. The method of claim 20 wherein the gellant is an aqueous solution of an alcohol chosen from the groups consisting of methanol, ethanol, i-propanol, t-propanol, t-butanol and mixtures thereof.
28. The method of claim 1 wherein the vinyl polymer is introduced into an aqueous solution of a gellant.
29. The method of claim 14 wherein the inactive gellant is activated by a trigger.
30. The method of claim 14 wherein the inactive gellant is a macromolecule.
31. The method of claim 30 wherein the active gellant comprises fragments of a macromolecule that are released by cleavage of the macromolecule.
32. The method of claim 31 wherein the cleavage of the macromolecule is enzymatic cleavage.
33. The method of claim 30 wherein the macromolecule is thermally denaturable.
34. The method of claim 30 wherein the macromolecule is collagen.
35. The method of claim 32 wherein the macromolecule is a physiological substrate of the enzyme.
36. The method of claim 35 wherein the macromolecule is selected from the group consisting of chondroitin sulfate, dermatan sulfate, keratan sulfate, hyaluronic acid, heparin, heparin sulfate and mixtures thereof and the enzyme is selected from the group consisting of chondroitinase ABC, chondroitinase

AC, chondroitinase B, testicular hyaluronidase, hyaluron lyase, heparinase I/III and mixtures thereof.

37. The method of claim 35 wherein the macromolecule is selected from the group consisting of biglycan, syndecan, keratocan, decorin, aggrecan, perlecan, fibromodulin, versican, neurocan, brevican and mixtures thereof and the enzyme is selected from the group consisting of, but not limited to, aggrecanase and mixtures thereof.
38. The method of claim 31 wherein the cleavage of the macromolecule is by irradiation with electromagnetic radiation or particulate radiation.
39. The method of claim 14 wherein the inactive gellant is a bad solvent sequestered in a vesicle, a liposome, a micelle or a gel particle.
40. The method of claim 39 wherein the liposome is a phototriggerable diplasmalogen liposome.
41. The method of claim 39 wherein the liposome undergoes a phase transition at about the body temperature of a mammal.
42. The method of claim 39 wherein the liposome comprises a mixture of dipalmitoylphosphatidylcholine and dimyristoylphosphatidylcholine.
43. The method of claim 39 wherein the gel particle releases its contents upon undergoing a phase transition at about the body temperature of a mammal.
44. The method of claim 39 wherein the gel particle comprises a polymer selected from the group consisting of poly(N-isopropyl acrylamide-co-acrylic acid), N-isopropylacrylamide, hyaluronic acid, pluronic and mixtures thereof.

45. The method of claim 39 wherein the gel particle releases its contents upon undergoing degradation.
46. The method of claim 1 wherein the gellant is more soluble than the vinyl polymer.
- 5 47. The method of claim 1 further comprising the step of processing the viscoelastic solution during the workability period.
48. The method of claim 47 wherein the step of processing includes injecting, molding or calendaring.
49. The method of claim 48 wherein the viscoelastic solution is injected into an  
10 actual or potential space in the body of a mammal.
50. The method of claim 49 wherein the viscoelastic solution is injected into an intervertebral disk or an articulated joint.
51. The method of claim 47 wherein the step of processing includes covering a burn or a wound.
- 15 52. The method of claim 1 wherein the viscoelastic solution further comprises one or more non-gelling components.
53. The method of claim 52 wherein the viscoelastic solution further comprises hyaluronic acid.
54. The method of claim 52 wherein the viscoelastic solution further comprises  
20 polyacrylic acid.
55. The method of claim 52 wherein the viscoelastic solution further comprises a therapeutic agent.

56. The method of claim 1 wherein the vinyl polymer solution further comprises at least one of nano or microparticulates to augment gelation.
57. A physically cross-linked gel produced by the method of:  
providing a vinyl polymer solution comprising a vinyl polymer  
5 dissolved in a first solvent;  
heating the vinyl polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl polymer;  
mixing the vinyl polymer solution with a gellant, wherein the resulting mixture has a higher Flory interaction parameter than the vinyl polymer  
10 solution;  
inducing gelation of the mixture of vinyl polymer solution and gellant;  
controlling the gelation rate to form a viscoelastic solution wherein workability is maintained for a predetermined period, thereby making a physically cross-linked gel.
- 15 58. The physically cross-linked gel of claim 57 wherein the step of providing a vinyl polymer solution includes the step of dissolving the vinyl polymer in the first solvent.
59. The physically cross-linked gel of claim 57 wherein the step of mixing the vinyl polymer solution with a gellant precedes the step of heating the vinyl  
20 polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl polymer.
60. The physically cross-linked gel of claim 57 wherein the vinyl polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl pyrrolidone and mixtures thereof.

61. The physically cross-linked gel of claim 60 wherein the vinyl polymer is highly hydrolyzed polyvinyl alcohol of about 50 kg/mol to about 300 kg/mol molecular weight.
- 5 62. The physically cross-linked gel of claim 60 wherein the vinyl polymer is highly hydrolyzed polyvinyl alcohol of about 100 kg/mol molecular weight.
63. The physically cross-linked gel of claim 57 wherein the vinyl polymer solution is about 1 weight percent to about 50 weight percent solution of polyvinyl alcohol based on the weight of the solution.
- 10 64. The physically cross-linked gel of claim 57 wherein the vinyl polymer solution is about 10 weight percent to about 20 weight percent solution of polyvinyl alcohol based on the weight of the solution.
65. The physically cross-linked gel of claim 57 further comprising the step of contacting the viscoelastic solution with a gellant.
- 15 66. The physically cross-linked gel of claim 57 wherein the gellant is active when mixed with the vinyl polymer solution.
67. The physically cross-linked gel of claim 57 wherein the gellant is inactive when mixed with the vinyl polymer solution.
68. The physically cross-linked gel of claim 67 wherein the step of inducing gelation of the viscoelastic solution includes the step of activating the gellant.
- 20 69. The physically cross-linked gel of claim 57, wherein the Flory interaction parameter of the mixture of vinyl polymer solution and gellant ranges from 0.25 to 1.0.



70. The physically cross-linked gel of claim 57 wherein the Flory interaction parameter of the mixture is about 0.25 to about 0.5.
71. The physically cross-linked gel of claim 57 wherein the Flory interaction parameter of the mixture is at least 0.5.
- 5 72. The physically cross-linked gel of claim 57 wherein the first solvent is selected from the group consisting of deionized water, dimethyl sulfoxide, an aqueous solution of a C1 to C6 alcohol and mixtures thereof.
- 10 73. The physically cross-linked gel of claim 57 wherein the gellant is selected from the group consisting of salts, alcohols, polyols, amino acids, sugars, proteins, polysaccharides, aqueous solutions thereof, and mixtures thereof.
74. The physically cross-linked gel of claim 73 wherein the gellant is selected from the group consisting of chondroitin sulfate, dermatan sulfate, hyaluronic acid, heparin sulfate and mixtures thereof.
- 15 75. The physically cross-linked gel of claim 73 wherein the gellant is selected from the group consisting of biglycan, syndecan, keratocan, decorin, aggrecan and mixtures thereof.
76. The physically cross-linked gel of claim 73 wherein the gellant is an alkali metal salt.
- 20 77. The physically cross-linked gel of claim 76 wherein the alkali metal salt is sodium chloride.
78. The physically cross-linked gel of claim 73 wherein the gellant is an aqueous solution of sodium chloride from about 1.5 molar to about 6.0 molar.

79. The physically cross-linked gel of claim 73 wherein the gellant is an aqueous solution of sodium chloride from about 2.0 molar to about 6.0 molar
80. The physically cross-linked gel of claim 73 wherein the gellant is an aqueous solution of an alcohol chosen from the groups consisting of methanol, ethanol, i-propanol, t-propanol, t-butanol and mixtures thereof.
81. The physically cross-linked gel of claim 57 wherein the vinyl polymer is introduced into an aqueous solution of a gellant.
82. The physically cross-linked gel of claim 67 wherein the inactive gellant is activated by a trigger.
83. The physically cross-linked gel of claim 67 wherein the inactive gellant is a macromolecule.
84. The physically cross-linked gel of claim 83 wherein the active gellant comprises fragments of a macromolecule that are released by cleavage of the macromolecule.
85. The physically cross-linked gel of claim 84 wherein the cleavage of the macromolecule is enzymatic cleavage.
86. The physically cross-linked gel of claim 83 wherein the macromolecule is thermally denaturable.
87. The physically cross-linked gel of claim 83 wherein the macromolecule is collagen.
88. The physically cross-linked gel of claim 85 wherein the macromolecule is a physiological substrate of the enzyme.

89. The physically cross-linked gel of claim 85 wherein the macromolecule is selected from the group consisting of chondroitin sulfate, dermatan sulfate, keratan sulfate, hyaluronic acid, heparin, heparin sulfate and mixtures thereof and the enzyme is selected from the group consisting of chondroitinase ABC, 5 chondroitinase AC, chondroitinase B, testicular hyaluronidase, hyaluron lyase, heparinase I/III and mixtures thereof.
90. The physically cross-linked gel of claim 85 wherein the macromolecule is selected from the group consisting of biglycan, syndecan, keratocan, decorin, aggrecan, perlecan, fibromodulin, versican, neurocan, brevican and mixtures 10 thereof and the enzyme is selected from the group consisting of, but not limited to, aggrecanase and mixtures thereof.
91. The physically cross-linked gel of claim 85 wherein the cleavage of the macromolecule is by irradiation with electromagnetic radiation or particulate radiation.
- 15 92. The physically cross-linked gel of claim 82 wherein the inactive gellant is a bad solvent sequestered in a vesicle, a liposome, a micelle or a gel particle.
93. The physically cross-linked gel of claim 92 wherein the liposome is a phototriggerable diplasmalogen liposome.
94. The physically cross-linked gel of claim 92 wherein the liposome undergoes a 20 phase transition at about the body temperature of a mammal.
95. The physically cross-linked gel of claim 92 wherein the liposome comprises a mixture of dipalmitoylphosphatidylcholine and dimyristoylphosphatidylcholine.

- 96 The physically cross-linked gel of claim 92 wherein the gel particle releases its contents upon undergoing a phase transition at about the body temperature of a mammal.
- 5 97. The physically cross-linked gel of claim 92 wherein the gel particle comprises a polymer selected from the group consisting of poly(NiPAAm-co-Aac), N-isopropylacrylamide, hyaluronic acid, pluronic and mixtures thereof.
98. The physically cross-linked gel of claim 92 wherein the gel particle releases its contents upon undergoing degradation.
- 10 99. The physically cross-linked gel of claim 57 wherein the gellant is more soluble than the vinyl polymer.
100. The physically cross-linked gel of claim 57 further comprising the step of processing the viscoelastic solution during the workability period.
101. The physically cross-linked gel of claim 100 wherein the step of processing includes injecting, molding or calendaring.
- 15 102. The physically cross-linked gel of claim 100 wherein the viscoelastic solution is injected into an actual or potential space in the body of a mammal.
103. The physically cross-linked gel of claim 102 wherein the viscoelastic solution is injected into an intervertebral disk or an articulated joint.
- 20 104. The physically cross-linked gel of claim 100 wherein the step of processing includes covering a burn or a wound.
105. The physically cross-linked gel of claim 57 wherein the viscoelastic solution further comprises one or more non-gelling components.

106. The physically cross-linked gel of claim 105 wherein the viscoelastic solution further comprises hyaluronic acid.
107. The physically cross-linked gel of claim 105 wherein the viscoelastic solution further comprises polyacrylic acid.
- 5 108. The physically cross-linked gel of claim 105 wherein the viscoelastic solution further comprises a therapeutic agent.
109. The physically cross-linked gel of claim 57 wherein the vinyl polymer solution is an aqueous solution of about 10 weight percent to about 30 weight percent polyvinyl alcohol based on the weight of the solution.
- 10 110. The physically cross-linked gel of claim 57 wherein the gellant is an aqueous solution of sodium chloride from about 1.5 molar to about 6.0 molar.
111. The physically cross-linked gel of claim 57 wherein the gellant is an aqueous solution of sodium chloride from about 1.5 molar to about 3.0 molar.
112. The physically cross-linked gel of claim 57 wherein the gellant is an aqueous  
15 solution of sodium chloride from about 1.75 molar to about 6.0 molar.
113. A physically cross-linked hydrogel substantially free of chemical crosslinkers.
114. A physically cross-linked hydrogel comprising at least about 10 weight percent polyvinyl alcohol solution gelled by immersion in about 2 to about 3 molar sodium chloride wherein the hydrogel is about 14 percent to about 21  
20 percent physically crosslinked.
115. The physically cross-linked hydrogel of claim 114 wherein the gel comprises about 12 to about 29 percent polyvinyl alcohol.

116. The physically cross-linked hydrogel of claim 114 wherein the vinyl polymer solution contains one or more non-gelling components.
117. The physically cross-linked hydrogel of claim 116 further comprising hyaluronic acid.
- 5 118. The physically cross-linked hydrogel of claim 116 further comprising polyacrylic acid.
119. The physically crosslinked gel of claim 116 further comprising a therapeutic agent.
- 10 120. The method of claim 1 wherein gelation is stopped by reducing the local concentration of the gellant.
121. The method of claim 120 wherein the local concentration of the gellant is reduced by diffusion.
122. A kit for providing vinyl polymer hydrogels to a region of interest comprising:  
15       a container of a vinyl polymer;  
         a container of a first solvent;  
         a container of a gellant; and  
         a delivery device.
123. The kit of claim 122 further comprising instructions for use.
124. The kit of claim 122 wherein the delivery device is a dispenser.
- 20 125. The kit of claim 122 wherein the dispenser further comprises a first chamber.
126. The kit of claim 122 wherein the dispenser further comprises a second chamber.

127. The kit of claim 122 wherein the dispenser further comprises a mixing chamber.
128. The kit of claim 122 wherein the dispenser further comprises a dispensing tube.
- 5 129. The kit of claim 122 wherein the dispenser further comprises at least one of a heater and cooler in communication with the dispensing chamber.
130. The kit of claim 122 wherein the dispenser further comprises at least one of a heater and cooler in communication with the mixing chamber.
131. The kit of 122 further comprising a temperature controller.
- 10 132. A method for sealing a defect in a soft tissue in a region of interest comprising the steps of:
- providing a first portion of a vinyl polymer hydrogel manufactured by:
- providing a vinyl polymer solution comprising a vinyl polymer dissolved in a first solvent;
- 15 heating the vinyl polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl polymer;
- mixing the vinyl polymer solution with a gellant, whereing the resulting mixture has a higher Flory interaction parameter than the vinyl polymer solution;
- 20 inducing gelation of the mixture of vinyl polymer solution and gellant;
- controlling the gelation rate to form a viscoelastic solution wherein workability is maintained for a predetermined period, thereby making a vinyl polymer hydrogel having the desired physical property;
- 25 and

providing a second portion of the vinyl polymer hydrogel having a high concentration level of the hydrogel.

133. An injectable hydrogel for nucleus pulposus augmentation manufactured by the method comprising the step of:

5                   providing a first portion of a vinyl polymer hydrogel manufactured by:  
                    providing a vinyl polymer solution comprising a vinyl polymer dissolved in a first solvent;  
                    heating the vinyl polymer solution to a temperature elevated above the melting point of the physical associations of the vinyl  
10                   polymer;  
                    mixing the vinyl polymer solution with a gellant, whereing the resulting mixture has a higher Flory interaction parameter than the vinyl polymer solution;  
                    inducing gelation of the mixture of vinyl polymer solution and  
15                   gellant;  
                    controlling the gelation rate to form a viscoelastic solution wherein workability is maintained for a predetermined period, thereby making a vinyl polymer hydrogel having the desired physical property;  
                    and  
20                   providing a second portion of the vinyl polymer hydrogel having a high concentration level of the hydrogel.

134. A method of controlling a property of a gel comprising:

                    dissolving a vinyl polymer in a first solvent to form a vinyl polymer solution; and  
25                   introducing the vinyl polymer solution in a volume of a second solvent to cause gelation, the second solvent having a higher Flory interaction parameter at a process temperature than the vinyl polymer solution.

135. The method of claim 134, wherein the Flory interaction parameter ranges from 0.25 to 1.0.



136. The method of claim 134 further comprising contacting the resulting gel with a suitable volume of the second solvent.
137. The method of claim 134 wherein the resulting gel has physical cross-linking.
138. The method of claim 134 wherein the step of introducing the vinyl polymer solution includes a plurality of cycles of dialyzing.
139. The method of claim 134 further comprising subjecting the gel to at least one freeze-thaw cycle.
140. The method of claim 134 wherein the vinyl polymer is highly hydrolized polyvinyl alcohol of about 50 kg/mol to about 300 kg/mol molecular weight.
141. The method of claim 134 wherein the vinyl polymer is highly hydrolized polyvinyl alcohol of about 100 kg/mol molecular weight.
142. The method of claim 134 wherein the vinyl polymer solution is about 1 weight percent to about 50 weight percent solution of polyvinyl alcohol based on the weight of the solution.
143. The method of claim 134 wherein the vinyl polymer solution is about 10 weight percent to about 20 weight percent solution of polyvinyl alcohol based on the weight of the solution.
144. The method of claim 134 wherein the first solvent is selected from the group consisting of deionized water, dimethyl sulfoxide, an aqueous solution of a C<sub>1</sub> to C<sub>6</sub> alcohol and mixtures thereof.
145. The method of claim 134 wherein vinyl polymer solution is introduced into an aqueous solution of a salt of an alkali metal.

146. The method of claim 145 wherein the aqueous solution is one of sodium chloride.
147. The method of claim 134 wherein the vinyl polymer solution is introduced into an aqueous solution of a C<sub>1</sub> to C<sub>6</sub> alcohol.
- 5 148. The method of claim 134 wherein the vinyl polymer solution is introduced into an aqueous solution of an alcohol chosen from the groups consisting of methanol, ethanol, i-propanol, t-propanol, t-butanol and mixtures thereof.
149. The method of claim 134 wherein the vinyl polymer solution is placed in a dialysis chamber having at least two sides having a membrane.
- 10 150. The method of claim 149 wherein the vinyl polymer solution is separated by the membrane from at least two different solvents.
151. The method of claim 150 wherein the vinyl polymer solution is separated by the membrane from a second solvent and a third solvent.
152. The method of claim 150 wherein the second solvent is an aqueous solution of sodium chloride from about 1.5 molar to about 6.0 molar.
- 15 153. The method of claim 151 wherein the third solvent is an aqueous solution of sodium chloride from about 2.0 molar to about 6.0 molar.
154. The method of claim 151 wherein the second solvent is a 0.0 molar aqueous solution of sodium chloride and the third solvent is an aqueous solution of sodium chloride from about 2.0 molar to about 6.0 molar.
- 20 155. The method of claim 149 wherein a gradient in chemical potential is formed across the vinyl polymer solution between at least two different solvents.

156. The method of claim 155 wherein a chemical gradient in chemical potential is formed across the vinyl polymer solution of about 4 mol. cm<sup>-1</sup>.
157. The method of claim 155 wherein a gradient of a physical property is formed across the gel that corresponds to the gradient formed across the vinyl  
5 polymer solution.
158. The method of claim 134 wherein the property is at least one of light transmission, gravimetric swell ratio, shear modulus, load modulus, loss modulus, storage modulus, dynamic modulus, compressive modulus, cross-linking, pore size.
- 10 159. The method of claim 155 wherein a gradient in the morphology of the gel corresponds to the gradient in the chemical potential.
160. The method of claim 150 wherein the different solvents are controlled in a temporal pattern to modulate the spatial gradient of a property of the gel.
161. The method of claim 134 wherein the vinyl polymer solution further  
15 comprises one or more non-gelling components.
162. The method of claim 161 wherein the gel further includes hyaluronic acid.
163. The method of claim 161 wherein the gel further includes polyacrylic acid.
164. A physically cross-linked gel produced by the method of comprising:  
dissolving a vinyl polymer in a first solvent to form a vinyl polymer  
20 solution;  
introducing the vinyl polymer solution in a volume of a second solvent to cause gelation, the second solvent having a higher Flory interaction parameter at a process temperature than the vinyl polymer solution.

165. The physically cross-linked gel of claim 164 wherein the vinyl polymer is polyvinyl alcohol having a molecular weight of about 50 kg/mol to about 300 kg/mol.
- 5 166. The physically cross-linked gel of claim 164 wherein the vinyl polymer solution is an aqueous solution of about 10 weight percent to about 30 weight percent polyvinyl alcohol based on the weight of the solution.
167. The physically cross-linked gel of claim 164 wherein the vinyl polymer solution is introduced in an aqueous solution of sodium chloride from about 1.5 molar to about 6.0 molar.
- 10 168. The physically cross-linked gel of claim 164 wherein the vinyl polymer solution is introduced in an aqueous solution of sodium chloride from about 1.5 molar to about 3.0 molar.
169. The physically cross-linked gel of claim 164 wherein the vinyl polymer solution is introduced in an aqueous solution of sodium chloride from about 1.75 molar to about 6.0 molar.
- 15 170. The physically cross-linked gel of claim 164 further comprising hyaluronic acid.
171. The physically cross-linked gel of claim 164 further comprising polyacrylic acid.
- 20 172. A physically cross-linked hydrogel substantially free of chemical crosslinkers.
173. A physically cross-linked hydrogel comprising at least about 10 weight percent polyvinyl alcohol solution gelled by immersion in about 2 to about 3

molar sodium chloride wherein the hydrogel is about 14 percent to about 21 percent physically crosslinked.

174. The physically cross-linked hydrogel of claim 172 wherein the gel comprises about 12 to about 29 percent polyvinyl alcohol.
- 5 175. The method of claim 173 wherein the vinyl polymer solution contains one or more non-gelling components.
176. The physically cross-linked hydrogel of claim 172 further comprising hyaluronic acid.
- 10 177. The physically cross-linked hydrogel of claim 172 further comprising polyacrylic acid.
178. An article of manufacture comprising a vinyl polymer gel having at least one gradient of mechanical properties.
- 15 179. A one-piece prosthetic intervertebral disk comprising a polyvinyl polymer hydrogel wherein the distribution of mechanical properties of the one-piece prosthetic intervertebral disk approximates the spatial distribution of the mechanical properties of the combination of the nucleus pulposis and the annulus fibrosis of the natural intervertebral disk.
180. The physically crosslinked gel of claim 164 further comprising a therapeutic agent.